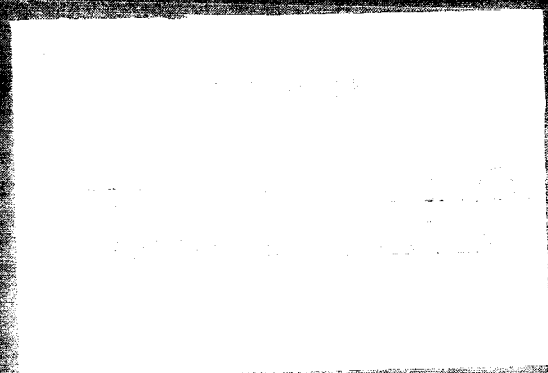
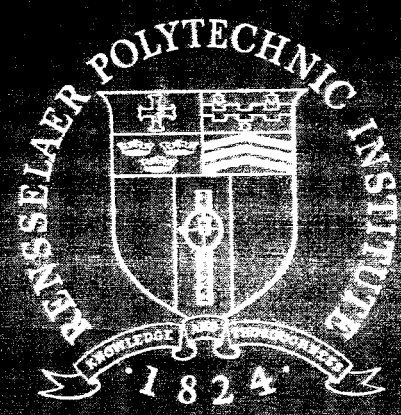
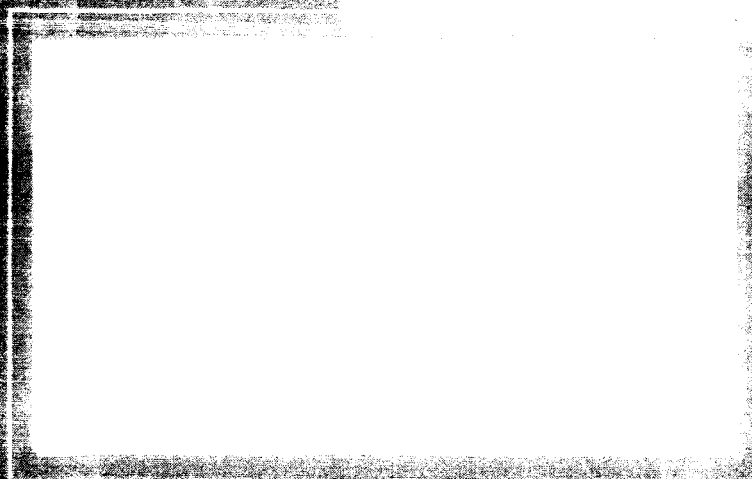


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Rensselaer Polytechnic Institute
 Troy, New York

SEMI-ANNUAL PROGRESS REPORT

**NATIONAL AERONAUTICS AND
SPACE ADMINISTRATION**

**GRANT NO.
NsG-100-60**

16

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**Rensselaer Polytechnic Institute
Troy, New York**

September 1964

Rensselaer Polytechnic Institute

Semi-Annual Progress Report
National Aeronautics and Space Administration Grant NsG-100-60
March 1, 1964 to August 31, 1964

INTRODUCTION

Eight new materials research projects were started and two projects were brought to a conclusion during this report period. Of the eight new projects, three developed from projects that have been supported since the inception of the program, they are the programs entitled, "Thermal Properties of Polymers," "Glass and Non-Metallic Materials" and "Spectroscopic Studies of Synthetic Reversible Oxygen-Carrying Chelates". The two programs that were concluded are entitled, "Excited Molecules" and "Charge Transfer Complexes". Progress reports from the new projects are included in the following pages as projects 470.29 through 470.36.

The new Materials Research Center, which is being financed by a 1.5 million dollar grant from NASA is nearing completion and occupancy in the near future is anticipated.

RESEARCH PROJECTS

Mechanical Properties of Polymers

470.05

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A. Fracture of Polymers

A criterion of fracture for semi-ductile, viscoelastic media has been formulated which has specific applicability to the ultimate properties of amorphous high polymers. The theory allows one to calculate the stress concentrations which exist at structural flaws or imperfections in the terms of the bulk macroscopic stresses applied to

a sample. By taking into consideration the viscoelastic time-dependent behavior of these stress concentrations, a plausible failure criterion for polymers has been developed.

Numerical solutions for the critical stresses developed adjacent to adventitious flaws have been developed for the specific case of isothermal growth of the plastically deforming regions. These solutions have been verified experimentally. Future work will be concerned with the adiabatic growth of the high stress regions which should be of importance in the prediction of fracture under high speed or impact loading conditions. The interconnections of constant strain rate, creep, and cyclical fatigue failure are also being considered in terms of the proposed theory (supported by the Institute of Paper Chemistry).

B. Polymer Network Mechanics

A generalized formulation of the relationship between the mechanical properties of a bulk, macroscopic body and the intrinsic properties of its constituent structural units has been obtained. This theory is based upon a prediction of the forces developed at the non-continuum structural level in terms of a criterion of minimum free energy.

Presently, the rubber elasticity network problem is being reconsidered in an attempt to develop appropriate constitutive equations for polymeric materials. The application of the theory to fibrous networks such as paper are also under investigation. Future applications of the theory may include mechanical descriptions of composite systems such as fiberglass reinforced phenolics. (Supported by the National Science Foundation.)

C. Viscoelastic Properties of Polymers

A dynamic mechanical spectrometer has been designed which is capable of producing forced tensile strains in polymeric materials from fractional cycles per second to ca. 2000 cps. In addition, dynamic forces of up to 25 pounds may be induced, and the samples may be preloaded with static elongations of up to several hundred percent. The equipment works equally well with either low compliance materials such as polystyrene or high compliance, rubberlike materials.

Experimental studies on the beta and gamma dispersions in polymethyl methacrylate, polystyrene, and polyvinyl alcohol-acetate copolymers are in progress. These studies are coordinated with the theoretical studies reported in parts A and B of this report.

Dielectric spectra obtained over a broad frequency and temperature range are also to be obtained on the samples used for dynamic mechanical studies.

The effects of solvent environments on the mechanical properties of various polymers are being studied through the use of a specially designed torsion pendulum. This device allows rapid measurements to be made of the viscoelastic parameters of a sample immersed in heated solvents or semi-solvents.

D. High Pressure Infrared Spectra

The pressure induced diminution of the symmetric stretching mode of the methylene groups in polystyrene, nylon, and polypropylene, as reported in a previous report, has been used to calculate a deformability

of the H-C-H angle. This value is circa 10 degrees per 20,000 atmospheres.

A Study of the Interaction of Dislocations with 470.09
the Discrete Second-Phase Particles in
Dispersion-Strengthened Alloys

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The objective of this program has been to delineate the effects associated with the presence of a distributed second-phase in a crystalline matrix by both theoretical considerations and experimental observations.

During this period, research efforts have centered principally upon experimental observations utilizing both replication and thin film transmission electron microscopy techniques. The specific areas investigated include:

A. Recovery and Recrystallization Kinetics in Two-Phase Systems

It has been well established that the presence of a distributed second-phase inhibits grain boundary migration, particularly secondary recrystallization in dispersion-strengthened alloy systems. Unfortunately, however, the mechanism by which this retardation occurs has never been delineated. Utilizing hot stage transmission electron microscopy and cine and sequence recording techniques, the rate of substructural recovery of cold worked structures and the interaction of migrating grain boundaries with second-phase particles have been studied. The alloy system investigated is the Al-Al₂O₃ SAP-type alloy. This alloy has afforded direct observation of these kinetic processes without the concomitant change in distributed phase structure which usually accompanies these high temperature processes. This study is currently in progress.

B. Work Hardening Behavior in Precipitation-Hardened Alloys

The role of the interface structure upon dislocation distributed phase interactions appears upon the basis of theoretical considerations, to be of prime importance in the development of substructure during deformation. Previously in this program, the substructural development in alloys containing noncoherent second-phase particles was studied. At the present time, the substructural development in an Al-Ag precipitation-hardened alloy is being followed by means of transmission electron microscopy.

In this alloy system, the matrix-particle interface structure can be varied by means of suitable heat treatment. This investigation is currently in progress.

C. Fracture Behavior

The influence of a distributed phase upon fracture mode and crack propagation is being studied utilizing the Al-Al₂O₃ SAP-Type alloy as a model alloy system. Replication studies of the fracture surfaces of these alloys broken in fatigue, appear to establish the mechanism by which dissolved gasses, particularly hydrogen, precipitate from solid solution due to the state of elastic stress in the aluminum matrix, due in turn to the constraint of the distributed second-phase. This study is still in progress.

D. Theoretical Studies

Theoretical studies of dispersion-strengthening based upon dislocation theory are progressing on a continuing basis.

Mechanisms of Solidification

470.10

Senior Investigator:

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Professor of Metallurgical
Engineering

Research Staff:

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Graduate Assistant

The effects of low frequency mechanical vibrations on nucleation of supercooled bismuth was continued. To prevent the breakdown of the silicone flux, which contaminated the bismuth, the crucible fixture was enclosed so that vibrating could be done with a nitrogen atmosphere over the flux.

The effects of ultrasonic frequency on nucleation of supercooled bismuth is being investigated. Frequencies of 2.25 and 5 megacycles are being used at present. Bismuth specimens of 90°C supercooling maintain this high degree of static supercooling when these frequencies are used, but specimens of lower static supercooling increase their degree of supercooling when vibrated with these frequencies. This is in opposition to the effect obtained at lower mechanical frequencies. It is planned to clarify the mechanism of the observed results and to study the effects of other frequencies on the nucleation of supercooled metals.

During the investigation of nucleation and growth of crystals in supercooled bismuth, two dendritic growth habits occurred on a single dendrite. The two growth habits are prismatic and triplanar. .

When the specimen was nucleated with a bismuth crystal, at a supercooling of about 15°C , triplane dendrites grew into the supercooled melt with some of the triplane dendrites twinning during growth. Each face of the triplane is a (110) plane (the indices are for a rhombohedral primitive unit cell) and each face of the triplane is serrated with the (110) planes being exposed on the striated surface triplane. In the rhombohedral system the (110) is also the twin plane. With a (110) plane as the exposed surface and a twin passing through this surface a prismatic dendrite can be nucleated and grow at any degree of supercooling up to 20°C .

The exposed surfaces of prismatic dendrite were (110) planes with one or more twins occurring, which are needed to sustain growth.

Ultrasonic Research

470.11

Senior Investigator: H.B. Huntington, Ph.D.
Professor of Physics

Research Staff: Z.P. Chang, B.S.
Research Assistant

Third order elastic constants for NaCl and KCl have been measured by observing the variation of acoustic velocities with uniaxial compression down a 111 axis. These results, in conjunction with Lazarus' values for the variation of elastic constants with hydrostatic pressure, determine 5 of the 6 third order constants. Because these results check one of the analogous third order Cauchy relations rather well, we have invoked the remaining two relations to remove the indeterminacy and to afford an estimate of all six constants. Of course there is no a priori reason to believe the Cauchy relations are exactly satisfied.

A secondary project is the measurement of the elastic constants of anthracene and naphthalene. A complete set for both have been obtained and are being rechecked.

Ultrasonic Pulse Interferometry

470.12

Senior Investigator: S. Katz, Ph.D.
Associate Professor
of Geophysics

Research Staff: Robert N. Schock, M.S.
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Through the use of a high pressure apparatus utilizing diamond anvils, solid-solid phase transitions in several materials were investigated using infrared spectrophotometric and visual microscopic

techniques. Of primary concern was the transition of calcite-aragonite under high pressure, as little is known either of the phase diagram of CaCO_3 , or the kinetics of the reaction over extended temperatures and pressures. In order to better understand the observation of phase transitions using infrared absorption to observe the change in structure, other compounds with known phase transitions were studied. These included AgI , KNO_3 and AgNO_3 . In the case of AgI , a slight shift to the red of approximately 1 micron of an absorption band was observed on increasing the pressure from 0 to 4 kb. The results of pressure runs on KNO_3 and AgNO_3 , were inconclusive. All of these compounds are still under study to check coordination changes during both displacive and reconstructive phase transition, and to study the correlation between absorption in the optical range and well-established phase transitions. Powdered synthetic CaCO_3 , and the naturally-occurring forms of iceland spar, aragonite, and Solenhofen limestone, as well as oriented single crystals of calcite, have been studied up to 10 kb, and structural changes have been observed. All reactions in this pressure range with these materials have been reversible and the small effects observed suggest that the structural changes are displacive in nature.

It has been found that the infrared apparatus now in operation will have to be modified to insure observation only of that part of the pressure field where pressures are nearly hydrostatic. A heating cell has been designed and built to fit into the diamond pressure cell. This will allow a temperature range of 20 -600°C to be studied under varying pressure. Studies of liquids under pressure have so far been handicapped by problems involved in finding a suitable gasketing material. It is believed that this problem has now been overcome and liquid-solid transitions can now be studied routinely.

Among the materials to be studied, in addition to calcium carbonate, are germania, and the rock forming silicates. Synthetic magnesium silicate and germanate are now being prepared. These materials form an isomorphous solid solution series, the silicate end of which is generally thought to be a major constituent of the upper mantle of the earth. Observations of polymorphic transitions, at pressures and temperatures attainable in the diamond-pressure cell, of the germanate end of the series and the dependence of these transition pressures on the mole fraction of silicate present, should permit extrapolation to possible phase transitions in the upper mantle.

Excited Molecules

470.14

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Graduate Assistant

A final report has been completed for project 470.14 and the contract terminated. The abstract is as follows:

The reactions of active nitrogen have been studied in a fast-flow, low-pressure system using a mass spectrometer whose leak was located directly downstream from the reaction zone. Reactions of metastable $N_2(A^3\Sigma_u^+)$ molecules, produced by means of surface catalyzed excitation, were also studied.

The results of the excited molecule experiments indicated that, in general, $N_2(A^3\Sigma_u^+)$ molecules do not play a major role in the reactions of active nitrogen with inorganic and organic substances such as: O_2 , O_3 , N_2O , C_2H_2 and C_2H_4 .

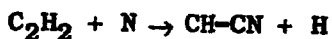
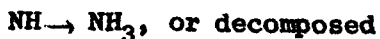
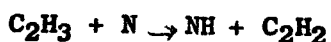
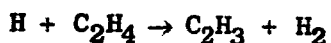
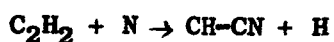
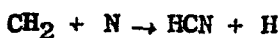
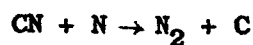
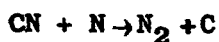
The reactions of N-atoms with hydrocarbons were studied along the lines of previous workers. It was found that, contrary to earlier work, HCN is not the only major nitrogen-containing product formed, but N_2 is also a substantial product. Under certain conditions, NH_3 and CH_3CN can also be major products. Ammonia added to the flame zone of the C_2H_2 -active nitrogen reaction was found to react with CH radicals formed, yielding HCN.

In general, the following observations were made:

1. Alkanes, especially CH_4 and C_2H_6 , react slowly with active nitrogen at room temperatures; the higher the alkane the greater the reaction rate;
2. alkenes react much faster than alkanes, but slower than acetylene;
3. some alkanes with weakly bound hydrogen atoms, viz, isobutane, react as rapidly as alkenes giving NH_3 , as well as HCN, as a major product under conditions where complete consumption of N-atoms occurs;
4. addition of HCl to the alkane reactions catalyzes the overall reaction and the rate then equals that of alkenes;
5. under optimum conditions, greater conversion of N-atoms to HCN, as measured by NO titration, can be obtained from CH_4 than with any other hydrocarbon.

From these results a general degradation mechanism is proposed involving the attack of the hydrocarbon, in general, by a radical other than the N-atom as the initial step. The N-atoms rapidly attack the primary products producing new radicals and both HCN and N_2 . The radicals then attach the hydrocarbons and the reaction proceeds, in many cases, over a chain-branching scheme.

This proposed reaction scheme, applied to C_2H_4 for demonstrative purposes, is as follows:

initiationpropagation

Other reaction mechanisms involving similar parallel reactions have been considered but the above scheme seems most plausible to explain the observed results.

A Ph.D. thesis has been submitted on this work to the Chemistry Department by D.R. Safrany.

The Relation of Molecular Structure and Intermolecular 470.15
Action in Flow of Polymers and Polymer Dispersions
as a Function of Temperature and Shear Rate

Senior Investigator:

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 Defense Education Act Fellow

The flow properties of several polybutadiene polymers are being investigated over a broad range of shear rates. The polymer samples being studied include; simple polybutadienes, carboxyl terminated polybutadienes and carboxyl terminated butadiene-nitrile copolymers. These polymers are currently of interest in serving as binders for heterogeneous solid materials.

Flow data has been recorded at shear rates of 0 to 20,000 sec.⁻¹ by cone-plate viscometry. Data at higher rates of shear (to about 100,000 sec.⁻¹) is now being obtained with a high pressure capillary viscometer.

The data obtained to date has been used to test Bueche's theory of flow for polymer melts, (the samples being used are liquids at room temperature) and to compare the activation energies of viscous flow to the chemical structures of the polymers.

Bueche's theory predicts that for linear coiling polymers, the flow characteristics for all melts should be the same, and that from a plot of log viscosity versus log shear rate the molecular weight can be calculated. The theoretically predicted log viscosity-log shear rate curve does not agree with experiment, but the curves of many different polymers have been shown to agree with one another and molecular weights calculated have been of proper magnitude. Our results agree with Bueche's experimental standard curve and give molecular weights of reasonable magnitude. Absolute values have yet to be determined.

The activation energies, Q_n , at zero shear rate separate into three groups: 1. simple polybutadienes with Q_n of 8.4 Kcal./mole, 2. carboxyl terminated polybutadienes with Q_n of 10.4 Kcal./mole 3. carboxyl terminated butadiene-nitrile copolymers with Q_n of 13.5 Kcal./mole. These differences are explained by the added resistance to flow caused by intermolecular hydrogen bonding between carboxyl groups and between carboxyl and nitrile groups.

At higher rates of shear the activation energies approach one another indicating the mechanical degradation of the intermolecular bonds.

High Temperature and Mechanical Metallurgy

470.18

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A. High Temperature Studies of Cobalt and Cobalt Base Alloys

A doctoral thesis concerned with the oxidation of cobalt in high-temperature, dehumidified, atmospheric-pressure oxygen has been completed. Parabolic weight-gain kinetics, measured by recording analytical balances, were determined at all temperatures of test.

Oxidation constants were computed and plotted as a function of $1/T$; this Arrhenius plot indicates that the kinetics of oxidation are controlled by differing activation processes at different temperatures. For $T < 700^\circ\text{C}$, $Q_3 = 31$ kcal/mole; for $700^\circ < T < 1120^\circ\text{C}$, $Q_2 = 48$ kcal/mole; for $T > 1120^\circ\text{C}$, $Q_1 = 29$ kcal/mole. Q_1 and Q_3 were found to be dependent upon the diffusion of Co through Co_3O_4 , with a diffusivity:

$$D = 6.75 \times 10^{-3} \exp (-48243/RT) \text{ cm}^2/\text{sec}$$

The change of kinetics at the Curie point was explained by a magnetic energy interaction between Co^{+2} ions in the lattice. Evidence of preferred orientation in the oxide film was found by x-ray diffraction techniques; the proposed orientation was also affected by the proposed magnetic interaction.

B. Experimental X-Ray Stress Analysis Procedures for Ultra High Strength Materials

X-ray stress analysis procedures have been developed for martenistic steels, in some cases further strengthened by ausforming and cold work, and for Maraging steels, each capable of achieving yield stresses of the order of 300,000 psi corresponding to elastic strains of the order of one-percent.

Exceptional results were obtained by the use of the two exposure method. Chromium characteristic radiation, filtered by vanadium foil, was used and a very satisfactory peak to background ratio of about 4:1 was obtained with the (211-121) martensite doublet.

A counting technique with the Geiger counter, combined with a least squares curve fitting procedure involving five points, was very satisfactory for precise locations of maximum intensity. Superior results were obtained when a multiplicative correction factor proposed by Koistinen and Marburger were applied.

Low Temperature Physics

470.19

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A. Ultrasonic Attenuation in Superconductors

The ultrasonic attenuation measurements are intended to determine the gap in the electronic energy levels in superconductors. The measurements in single crystals of lead have been complicated by the presence of a previously unreported amplitude dependence of the attenuation. By working at very low amplitudes we have found a gap at the absolute zero of temperature of $(4.1 \pm .2) \text{ K Tc}$ for lead. This value is in agreement with other methods of determination but disagrees with earlier measurements using the present method. It seems likely that the amplitude dependence misled earlier researchers. Studies on this dependence are continuing. Thus far it appears to occur only in the superconducting state and to be unrelated to harmonic generation or acoustic velocity changes. Measurements on other samples of lead and other superconductors are planned.

B. Superconductivity and Lattice Defect

The resistance minimum reported in the previous semi-annual report has been further investigated. It has been possible to generate this anomalous return toward superconductivity by plastic deformation at 4.2°K of several alloys of indium in lead. Over the range of 2 to 20 weight percent indium, the strain dependence does not appear to vary appreciably but the annealing is quite different. Perhaps the most startling observation to date is that straining of alloys of several percent lead in indium does not seem to bring on the minimum, although this is still a preliminary result. If this is confirmed by further observations it will suggest a dependence upon crystal structure, the indium structure differing from that of lead by an 8% extension of one axis. Studies of the dislocation structure and straining mechanisms in indium will be in order. In addition investigations on aluminum alloys, which will have the same structure as the lead alloys, are planned.

Ceramics Research

470.20

Senior Investigator:

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 R. Haskell, B.Met.E.
 Graduate Assistant
 D. Hibbard
 Technical Assistant

A. Current Research

The study of the anisotropy of the oxygen ion polarizability in BaTiO_3 and the incorporation of the data into the theoretical molecular model of BaTiO_3 has been completed and has resulted in quite good agreement between theory and experiment. A zero wall thickness was found for both (010) and (220) type 180° domains, and the calculated wall energies were found to be 1.52 and 10.3 ergs/cm², respectively. This study was the Ph.D. thesis work of W. Lawless, and four publications have resulted. This concludes the work on 180° domain walls and the nature of ferroelectricity in BaTiO_3 .

An attempt was made to reinforce an aluminate glass with sapphire whiskers. With hot-pressing techniques a hard (8 on Mohs' Scale) compact was prepared, but the role of the whiskers is uncertain because of problems with reaction with the whiskers.

Equipment has been constructed for deforming BaTiO_3 crystals while on the microscope stage so that the deformation twinning behavior can be studied.

B. Future Research

Besides continuing the BaTiO_3 deformation studies, we have begun a program to obtain quantitative information regarding the kinetics of reduction of Al_2O_3 with H_2 . Curves of weight loss versus time will be obtained for reduction in hydrogen of various moisture contents and partial pressures. This information should give understanding regarding the oxide vapor species of Al and the growth of sapphire whiskers. This work will be extended to cover the vaporization of ruby in the same environments.

Dispersion-Strengthened Materials

470.23

Senior Investigator:

F.V. Lenel, Professor of
 Metallurgical Engineering

Research Staff:

G. Leverant, Research Fellow
 J. Hirschhorn, Research Fellow
 H. Nayar, Graduate Assistant
 M. Singh, Graduate Assistant

In an effort to elucidate the strengthening mechanism found in internally oxidized silver-magnesium alloys, emphasis is being put on the following three experimental approaches:

1. The study of alloys by transmission electron microscopy is in progress. Techniques of producing films of the alloys thin enough so that electrons can penetrate them are being perfected. Alloys which have been internally oxidized at different temperatures, at different rates of advance of the oxidation boundary, and which have been subjected to different annealing treatments are to be studied by this technique in order to find under which conditions structural features are developed which can be identified either in electron transmission or electron diffraction of thin films.

2. An apparatus for the determination of the elevated temperature creep behavior of wires of internally oxidized silver magnesium alloys has been built and creep tests are underway.

3. A technique for producing single crystal silver-magnesium alloy specimens is being developed. These single crystals are to be internally oxidized under various conditions and their plastic properties (critical resolved shear stress and flow stress) are to be determined.

An investigation of dispersion strengthening in ice has been started. Colloidal gold and colloidal silica are the second phases. Methods of producing fine dispersions are being developed. Up to now only hardness has been used to characterize the dispersions, but it is expected that eventually tensile and creep properties will be measured.

Metal Dissolution at Very High Applied Currents 470.25

Senior Investigator: N.D. Greene, Associate
Professor of Metallurgical
Engineering

Research Staff: H. Cleary, Graduate Assistant

The purpose of this program is to determine the basic corrosion and electrochemical characteristics of iron and iron alloys (steels). Although the corrosion behaviors of iron and commercial steels have been empirically determined by conventional corrosion tests, few studies have been devoted to determining the effect of metallurgical variables on electrochemical properties. Composition and/or structure have a pronounced effect on chemical behavior as evidenced by the wide variations observed between nearly identical samples.

A literature survey on this topic has been completed. Future plans include the following measurements with both commercial steels and special iron alloys prepared from high purity materials:

1. Hydrogen overpotential as a function of composition, heat treatment and grain size.

2. Anodic dissolution measurements to determine the mechanism of the frequently observed hysteresis effects.
3. Effect of environmental variables (composition, temperature and agitation) on electrochemical characteristics.

Nuclear Magnetic Resonance Research

470.26

Senior Investigator: P.A. Casabella, Ph.D.
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Research Staff: J.M. Marsh, Jr., M.S.
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T. Oja, B.S.
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H.M. Weiskittel, B.S.
Oak Ridge Institute of
Nuclear Studies Fellow

The study of the ferroelectric behavior of Rochelle salt by means of nuclear magnetic resonance (NMR) techniques has been continued. It has been observed that the two different types of domains that are present in Rochelle salt can be distinguished by NMR techniques. In the crystals being studied, one of these domains was the more stable of the two, when this work was begun, but now the other type has become more stable. The reason for this change is being investigated.

In addition to this work, a new program of investigating alkali halide crystals has been begun. The object of this work is to measure the distortion of the ions in the solid due to a compression of the crystal. This will be accomplished by compressing the crystals a known amount and observing the effect on the NMR. In addition the effect expected on the NMR if the ions do not distort will be calculated. The difference between the observed and predicted values will then be used to determine the ionic distortion.

X-Ray Scattering

470.28

Senior Investigator: J.L. Katz, Ph.D.
Associate Professor of Physics

Research Staff: R.H. Wilson
Graduate Assistant
E.F. Skelton,
Graduate Assistant
L.H. Vogt, Jr.
NASA Pre-Doctoral Trainee

The studies of the temperature dependence of Debye Temperatures in metals and alloys is being extended to new systems as well as down to liquid Helium temperatures. In addition thermal diffuse x-ray scattering studies are being initiated. The study of the Fe-Ni system in the inner region is at present under support of a research grant from the Army Research Office (Durham). A progress report on this work (which comprises the Ph.D. dissertation of Dr. R.H. Wilson) has been submitted to NASA.

A second continuing effort is in the field of x-ray crystal structure studies of Ruthenium - SO₂ coordination compounds. Infra-Red spectral studies in this field had been previously initiated by Professor S. Wiberley of the Chemistry Department. This interdisciplinary effort came to fruition with the presentation of a paper entitled, "The Crystal and Molecular Structure of RU - SO₂ Complexes: I (Ru^{II} (NH₃)₄(SO₂) Cl)Cl" by Lester H. Vogt, Jr., J. Lawrence Katz and Stephen E. Wiberley at the annual meeting of the American Crystallographic Association held at Montana State College in July. The work comprises the Ph.D. dissertation of Dr. Lester H. Vogt, Jr. Preliminary data on the bromo-bromide compound show that it is isostructural with the chloro-chloride compound. Full 3 dimensional data are now being collected and prepared for structure refinement. Several other complexes have been studied by powder diffraction techniques. It is anticipated that further x-ray studies on these complexes will be correlated with the parallel infra-red studies.

Thermal Properties of Polymers

470.29

Senior Investigator:

D. Hansen, Ph.D.
Assistant Professor of
Chemical Engineering

Research Staff:

J.A. Rusnock, Ph.D.
Research Assistant
B. Washo, B.S.
N.D.E.A. Fellow
N. Watkins, B.S.
Graduate Assistant
R. Kantayya, B.S.
Graduate Assistant

A. Thermal Properties

An apparatus has been constructed and tested which will permit measurement of the thermal conductivity on oriented polymers and elastomers in tension. This apparatus will be used initially to study anisotropy in the thermal conductivity of oriented polystyrene, polymethylmethacrylate and polyisoprene. Hopefully, the thermal conductivities will be related theoretically to molecular orientation characterized by birefringence measurement.

Some further data on the thermal conductivity of polystyrene

as a function of molecular weight are being obtained. These will supplement earlier measurements on the same subject.

B. Structure

The techniques developed in this laboratory for thin sectioning and metal staining polymers for electron microscopy are being applied to a study of crystallization in polyoxymethylene and polyethylene-terephthalate. For various reasons most studies of polymer crystallization have been made on thin films or solutions. In this study, the effects of temperature and cooling rates on the crystalline morphology of bulk samples are being studied.

Previous studies on nylon-66 filaments in this laboratory led to a proposed description of the mechanism of neck-drawing. This description has been generalized to the mechanism of cold-drawing in crystalline polymers. Optical studies of the cold-drawing process are now being made on several crystalline polymers including polyethylene and polypropylene.

Glass and Non-Metallic Materials

470.30

Senior Investigator:

J.D. Mackenzie, Ph.D.
Professor of Materials Science

Research Staff:

R. Hakim
Graduate Assistant
A. Dix
Graduate Assistant
M. Schwartz
Graduate Assistant
R. Mehalso
Graduate Assistant

The objectives of this work are twofold: (a) to correlate properties and structures of glasses and other non-metallic solids, and (b) to prepare new materials and study their properties.

During this period, experimental work was started on preparation and electrical properties of semiconducting oxide glasses. Work on the crystallization of BeF_2 glasses and diffusion of Ca in CaO SiO_2 is in progress, and studies on ceramic-metal interfaces have begun.

Vibrational Spectroscopy Inorganic Substances
in the Vapor Phase

470.31

Senior Investigator: S.C. Wait Jr., Ph.D.
Associate Professor of
Physical Chemistry

Research Staff: G. Kelly
Graduate Assistant

Investigations of the infrared spectra of inorganic substances in the vapor phase are being undertaken for the purposes of (1) making vibrational assignments and normal coordinate analyses, (2) studying the stability of inorganic ions at high temperatures, (3) studying ionic interactions leading to polymeric species in the vapor phase and (4) investigating models to represent the behavior of the substances. Work to date has been centered on design and construction of high-temperature infrared cells, including a study of the stability of IRTAN-4 windows at elevated temperatures. The latter study showed that these windows are not suitable for use at elevated temperatures. Accordingly sodium chloride windows are being used. Immediately upon completion of the cell construction, spectroscopic studies will start together with an intensive investigation of the ionic model. Initial theoretical attention will be devoted to the Rittner¹ model.

Irreversible Thermodynamics of the Solid
State of Linear High Polymers

470.32

Senior Investigator: B. Wunderlich, Ph.D.
Associate Professor of Chemistry

Research Staff: E. Hellmuth, Ph.D.
Post-Doctoral Fellow

The method of fast heating to avoid irreversible and irreproducible reorganization in polymers during thermal analysis, termed zero entropy production melting, has been investigated further. In particular, its upper heating rate limit has been established. On faster and faster heating rates, the melting rate is slower than the addition of heat, so that superheating results. This superheating and its dependence on molecular weight, crystal perfection, and crystal morphology was established for polyethylene and polytetrafluoroethylene.

For the next period a continuation of this work on irreversible processes on melting is planned as well as specific heat measurements using the newly acquired calorimeter.

1

E.S. Rittner, J. Chem. Phys., 19, 1030 (1951) and E.J. Finn, J. Chem. Phys., 39, 2423 (1963).

Ultra-Low Temperature Solid State Physics Research 470.33

Senior Investigator: G.L. Salinger, Ph.D.
Assistant Professor of Physics

Research Staff: R.J. Ascutto
Graduate Assistant

The purpose of this project is to measure magnetic interactions in dilute magnetic salts at very low temperatures. The project has just been initiated. We are constructing a sensitive mutual inductance bridge and a resistance bridge capable of making measurements with power inputs of the order of 10^{-12} watts. A design for a He³ refrigerator is under way.

We plan to finish and test the electronic apparatus and put the He³ refrigerator in operation during the next semester. A suitable series of crystals will be grown and the interactions studied.

Thermal Decomposition of Inorganic 470.34
Coordination Compounds

Senior Investigator: R.A. Bailey, Ph.D.
Associate Professor of
Inorganic Chemistry

Research Staff: F. Montillo
Research Assistant
I.R. Feins
Research Assistant

The objectives of this study are to investigate the manners in which coordination compounds containing organic ligands decompose, in order to obtain more information on the effect of the metal atom on the ligand.

The first six-month period of this project has been spent partly in developing apparatus for thermogravimetric studies. Not all of the necessary components have been delivered at this time. In the meantime, some compounds have been prepared for investigation. These involve metal-oxygen or metal-nitrogen bonds with fairly simple organic structures, based on ureas and oximes. Some preliminary differential thermal analysis studies of these are about to begin.

Thermodynamics and Kinetics Vaporization
Processes for Inorganic Materials

470.35

Senior Investigator: H. Wiedemeier, Ph.D.
Assistant Professor of Chemistry

Research Staff: None

Research on the kinetics and thermodynamics of vaporization processes for inorganic materials is proposed, specifically for compounds of transition metals and Group VI elements. These studies will be extended to the investigation of III-V compounds which have gained considerable technological importance during the last decade.

It is proposed to develop this research program along three main lines:

1. Preparation of pure single crystals.
2. Vaporization studies under equilibrium and non-equilibrium conditions.
3. Correlation of obtained results with structural properties of the investigated materials.

In the case of the III-V compounds emphasis will be placed on the investigation of the properties of the solid materials with special consideration of the electrical and optical properties of these materials.

The Senior Investigator of this project arrived at Rensselaer in August 1964. Some basic equipment has been ordered and work is just starting. It is expected that a manifold will be constructed and equipment will be tested during the next period.

Spectroscopic Studies of Synthetic
Reversible Oxygen-Carrying Chelates

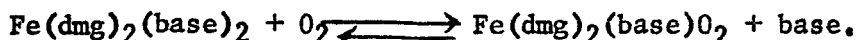
470.36

Senior Investigator: S.E. Wiberley, Ph.D.
Professor of Chemistry

Research Staff: M. A. Faigenbaum
Assistant Professor of Chemistry

Iron (II) dimethylglyoxime ($\text{Fe}(\text{dmg})_2$) is the first synthetic oxygen-carrying chelate reported that does not contain cobalt as the coordinating atom. Fifty percent aqueous dioxane solutions of this complex, containing such added bases as pyridine, ammonia, histidine

or imidazole, and held within a pH range of 7-11, exhibit the following reversible reaction with oxygen:



Both the forward and the reverse reaction can be followed by changes in the solution's absorption spectrum (1), however, the reversible oxygen-carrying properties of solid Fe(dmg)_2 have not been studied.

H. Nouguchi of the Tokyo Institute of Technology has reported the isolation of solid Fe(dmg)_2 by the removal of base molecules from $\text{Fe(dmg)}_2(\text{base})_2$ (2). The same investigator also reported the use of solid Fe(dmg)_2 as a catalyst in the production of polymers. (3)

The object of our work is to prepare and to study solid Fe(dmg)_2 as a possible synthetic reversible oxygen-carrying chelate. Of special interest is the effect of such oxygen exchange on the infrared spectra of the compound, for such a study might provide information on the nature of the structure and bonding in the chelate.

The precursors of Fe(dmg)_2 , $\text{Fe(dmg)}_2(\text{py})_2$ (py = pyridine) and $\text{Fe(dmg)}_2(\text{NH}_3)_2$, were prepared according to the method of Tschugaeff (4), i.e., an alcoholic solution of dimethylglyoxime and pyridine (or ammonia) was added to an aqueous solution of FeSO_4 and the precipitated complex collected by means of suction filtration. Neither complex could be recrystallized from either its respective base or alcoholic solutions of its respective base. Both $\text{Fe(dmg)}_2(\text{py})_2$ and $\text{Fe(dmg)}_2(\text{NH}_3)_2$ were isolated as dark brown crystalline solids.

According to Noguchi's method (2), an attempt was made to obtain Fe(dmg)_2 by heating $\text{Fe(dmg)}_2(\text{py})_2$ in vacuum but without success. Different ways of combining the reagents in the preparation of $\text{Fe(dmg)}_2(\text{py})_2$ (i.e. addition of a mixture of dimethylglyoxime and pyridine to Fe^{++} ; addition of a mixture of dimethylglyoxime and Fe^{++} to pyridine; addition of a mixture of pyridine and Fe^{++} to dimethylglyoxime) did not yield products which could be converted to Fe(dmg)_2 .

Future work will involve other preparative techniques for these complexes. Efforts will be directed toward more complete removal of pyridine or ammonia from the complexes, an operation which so far proves to be quite difficult. The x-ray diffraction pattern of these complexes will also be investigated.

1

Drake, J.F., and Williams, R.I., *Nature*, **182**, 1084 (1958).

2

Noguchi, H., private communication.

3

Noguchi, Hiromichi and Kambara, Shu, Catalyst Systems and Their Application to the Polymerization of Phenylnlacetylene, *J. Polymer Science, Part B. Polymer Letters* **1** #10 553 (1963).

4

Tschugaeff, L., On Complex Compounds of Oximes, *Z. Anorg. Chem.*, **46**, 144 (1905).

TECHNICAL PAPERS

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Submitted to Acta Metallurgica

Nissan, A.H., Sternstein, S.S.

"Cellulose Bonding"

Submitted to Tappi in September 1962.

25 copies of reprint submitted to NASA

Hansen, D., Rusnock, J.A.

"The Mechanism of Cold-Drawing in Crystalline High Polymers"

Submitted to Journal of Applied Physics

Dromsky, J.A., Lenel, F.V.

"The Influence of Thermal Treatments Upon the Microstructure and Mechanical Properties of Aluminum-Aluminum Oxide Alloys"

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Lawless, W.N., DeVries, R.C.

"Anisotropic Oxygen Polarizability in Carbonate Minerals"

Submitted to Journal of Physics and Chemical Solids

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"The Temperature-Dependence of the Reflective Index of Tetragonal BaTiO_3 by a Modified Chaulnes' Method"

Submitted to Journal of Applied Physics

Haskell, R.W., DeVries, R.C.

"Estimate of Free Energy Formation of Kyanite"

Submitted to Journal of American Ceramic Society

Rusnock, J.A., Hansen, D.

"The Application of Transmission Electron Microscopy to Polymer Thin Sections. I. Observations on Nylon-66, Bulk and Filament Forms"

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Hansen, D., Chong, C. Ho

"Thermal Conductivity of High Polymers"

To be submitted to the Journal of Polymer Science

Lawless, W.N.

"On the Oxygen Polarizability in BaTiO_3 and Related Materials"

To be submitted to Physical Review

Technical Papers (continued)

Lawless, W.N.

"Anisotropic Oxygen Polarizability and The Lorentz
Correction in BaTiO_3 "

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Schenck, J.F., Willis, J.S., Shaw, R.W.

"Effects of Helium Temperature Strain on
the Superconducting Transition of Pb-In Alloys"

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Casabella, P.A.

"Nuclear Magnetic Dipole Coupling in Solid BF_3 "

Submitted to the Journal of Chemical Physics

Katz, J.L., Wilson, R.H.

"The Use of X-Ray Scattering to Study the Anomalous
Elastic Properties of Fe-Ni Alloys"

Submitted to Acta Crystallographia

APPENDIX A

Members of Interdisciplinary Materials Research Center
Faculty Committee

S. E. Wiberley, Chairman	Professor of Analytical Chemistry and Dean of the Graduate School
G. S. Ansell	Associate Professor of Metallurgical Engineering
W. H. Bauer	Professor of Physical Chemistry and Dean of the School of Science
A. A. Burr	Professor of Metallurgical Engineering and Dean of the School of Engineering
R. H. Hartigan	Director of the Research Division
H. B. Huntington	Professor of Physics, Chairman of the Department of Physics
G. J. Janz	Professor of Physical Chemistry
F. V. Lenel	Professor of Metallurgical Engineering
S. S. Sternstein	Professor of Chemical Engineering
J. M. LoGiudice	Administrative Director of the Interdisciplinary Materials Research Center